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A comparative study of individual and simultaneous evaluation of kinetic measurements

Summary of the PhD thesis

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1. Introduction

Evaluation of kinetic data is based on techniques that have been widely accepted among the scientists long ago. The method of initial rates and curve-by-curve exponential fitting have almost been exclusively utilized to unravel the mechanism of reaction systems. In order to fit these curves with mathematical exactness with a function the transformation of the primary data became necessary, i.e. if the function between the relationship between the measured signal and the concentration could have been transformed into a linear relationship. The data obtained this way could easily be fitted with a straight line with more simple tools. The linear relationship then could be transformed back to its original form and the fitted parameters, their transformed equivalents and the specific combination of them gave the final rate constant(s). The mechanism of simple chemical systems studied initially could be determined with high probability using the methods mentioned above.

A literature survey revealed that most of the chemists dealing with chemical kinetics use these simplified evaluation techniques, although the incautious use of these methods may easily lead them into pitfalls, and even help other chemists to derive false assumptions through publication of the faulty results. I have searched the publications of such noted journals for the keywords "pseudo-first order" and "initial rate" as Journal of the American Chemical Society, Journal of Physical Chemistry A and B and Inorganic Chemistry from 1997 to 2007. The search gave more than 3000 hits, which also shows that the major role is still played by these simplified evaluation techniques.

Chapter 2 of the thesis summarizes the literature background of the two real chemical systems. In connection with the iron(III)–sulphate system I have found very few publications, which mainly focus on the equilibrium studies, or emphasize the need for exactly determined stability constants which were not available at the time of publication. Only two papers dealing with kinetic measurements have been published in the 1950s, which are very important. However the authors of these publications could rely on only the simplified evaluation techniques.

Their results are still sound, despite the fact that the available concentration ranges have been restricted due to the usage of simplified evaluation methods. In fact the applied restrictions themselves caused that the system did not present such phenomena which could have led the chemists into pitfalls. This duality still exists, if the method of pseudo–first order is about to be used. All the facts mentioned above inspired me to clarify the equilibrium and kinetic description of the system.

Hypochlorous acid – chlorite system came into the focus of interest of chemists when studying chemical oscillators. Its kinetics have been described in the 1980s, and a mechanism has been suggested which was elaborated using the most state-of-the-art evaluation technique available at that time. During the past decades new results have came upon – namely the catalytic role of chloride – which made it important to refine and further develop the mechanism suggested.

The stunning results of the literature search presented above prompted me to elaborate simplified models based on real kinetic systems, on which the difference between the results obtained by simplified evaluation techniques and simultaneous curve fitting can be shown even better.

Each of the models presented are based on such real chemical system that have been studied by numerous internationally acknowledged research groups. In many cases the mechanism obtained by individual curve fitting has been disproved by the usage of simultaneous curve fitting.

During the elaboration of the models it was important for me to give the largest variety of examples for the types of mechanisms that may show up in real systems, and to emphasize the possible pitfalls of the utilization of both individual exponential fitting and the method of initial rates.

2. Experimental methods

I have clarified the equilibrium composition of iron(III)–sulphate system first using spectrophotometry at $25.0 \pm 0.5°C$ temperature and at 1.0 M ionic strength. The measurement was planned and the data was evaluated using the program PSEQUAD. In order to determine the number of absorbing species from the absorbance matrices with linear algebraic methods I have used the MRA and M^3 programs. The kinetic measurements were carried out at 25.0 ± 0.5 °C temperature and at 1.0 M ionic strength using „stopped-flow" spectrophotometric technique. For the evaluation of the kinetic curves the ZiTa multipurpose program package was used.

In the hypochlorous acid–chlorite system I have studied the chloride concentration dependence of the reaction rate with spectrophotometric method at 0.5 M ionic strength. The evaluation of the data was done using the previously mentioned ZiTa program package.

The experimental data of the model systems was simulated using the ZiTa package. The superposition of experimental error of Gaussian distribution was done by a program written by myself. The curves prepared this way were fitted one-by-one with exponential functions using the AXUM technical plotting and data processing software.

3. New scientific results

Iron(III)–sulphate system

1. I have studied the hydrolytic equilibrium of the iron(III)-ion at T(Fe^{3+}) = 0.1574–0.6296 mM and T(H^+)=1–100 mM concentration range at 1 M ionic strength in aqueous solution. Among these conditions the formation constant of $Fe(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$ could be determined $10^{-2.836\pm0.010}$ and $10^{-2.939\pm0.074}$ respectively.

2. I have determined the equilibrium composition and the formation constants of the sulphate containing species in the iron(III)–sulphate system. Among these condition the formation constant of $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe(SO_4)^+$ and $Fe(SO_4)_2^-$ could be determined $10^{-2.843\pm0.012}$, $10^{-2.880\pm0.080}$, $10^{-2.324\pm0.020}$ and $10^{-3.834\pm0.030}$ respectively.

3. On the basis of the results of the kinetic studies I have made a suggestion for the possible mechanism of the system by nonlinear parameter estimation. The most important feature of the mechanism is that it does not obey the theory of stepwise complex formation applied in equilibrium chemistry. The key step of the bisulphate complex formation is the

$$2FeSO_4^+ \rightleftharpoons Fe^{3+} + Fe(SO_4)_2^-, \tag{1}$$

   equilibrium, which is fast in both directions and only a lower minimum value of its rate constants can be determined.

4. I have also fitted the experimental curves individually with exponential functions. Using this evaluation technique I was unable to determine an acceptable mechanism. The plot of the pseudo-first order rate constants versus ligand concentration gave straight lines which had different pH dependent intercepts and the fitted straight lines had a common crossing

point on the x axis outside of the origin. All these findings led to the conclusion that the mechanism the system could be described with is more complex than it could be determined with individual curve fitting and linearization.

Hypochlorous acid – chlorite system

5. I have given the explanation of the catalytic effect of chloride ion through the

$$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O \tag{2}$$

equilibrium. This process in fact can be further split into two equilibria with the help of the Cl_2OH^- species according to the equations below

$$HOCl + Cl^- \rightleftharpoons Cl_2OH^- \tag{3}$$

$$Cl_2OH^- + H^+ \rightleftharpoons Cl_2 + H_2O \tag{4}$$

The increased reactivity of Cl_2OH^- compared to HOCl and back production of chloride ion through its reactions explains the effect that chloride ion increases both the initial rate of the formation of chlorine dioxide and changes the chlorine dioxide yield in HOCl and chlorite excess as well.

6. On the basis of the results of the nonlinear parameter estimation I have found the HOCl catalysed decomposition of Cl_2O_2 intermediate more justified, compared to the spontaneous hydrolysis. Thus the catalysed path became the main route of chlorate formation.

Simulated model systems

7. I have proven through model **A**, that an important route can be lost in case of branching mechanisms in case of incautious use of individual curve fitting.

8. I have shown with the help of model **B**, that a two step complex formation may be erroneously identified as a one step process, in case the data obtained exclusively from individual curve fitting method. If exact equilibrium measurements had been carried out beforehand, the complete mechanism could have been determined using individual curve fitting.

9. In model **C** I have demonstrated that in case of systems measured with stopped-flow technique and evaluated according to the well-known methods, a two step complex formation can be identified as a one step reaction. The complete mechanism in this case is impossible to be determined even if equilibrium measurements have been done.

10. I have emphasized the shortcoming of the initial rates method through model **D**. The rate determining step may be erroneously identified as pH dependent if the pH dependence of the final stoichiometry is ignored.

Publications

1. **B. Kormányos**, I. Nagypál, G. Peintler, A. K. Horváth
Effect of chloride ion on the kinetics and mechanism of the reaction between chlorite ion and hypochlorous acid.
Inorganic Chemistry, 2008, 47(17):7914-20. IF : 4, 147

2. **B. Kormányos**, G. Peintler, A. Nagy, I. Nagypál
Peculiar kinetics of the complex formation in the iron(III)-sulfate system
International Journal of Chemical Kinetics, 2008, 40(3):114-124 IF : 1, 370

3. **B. Kormányos**, A. K. Horváth, G. Peintler, I. Nagypál
Inherent pitfalls in the simplified evaluation of kinetic curves.
Journal of Physical Chemistry A., 2007, 111(33):8104-9. IF : 2, 918

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Conference lectures, posters

1. I. Nagypál, **B. Kormányos**, G. Peintler, A. K. Horváth
   Inherent pitfalls in the simplified evaluation of kinetic curves.
   233rd ACS National Meeting, 2007, Chicago, IL, USA, (lecture)
   Lecture & Abstract, Abstract Inor-851

2. **B. Kormányos**, A. Horváth, G. Peintler, I. Nagypál
   Az egyszerűsített kiértékelési módszerek kelepcéi a reakciókinetikában
   MTA Reakciókinetikai Munkabizottsági ülés, 2007, Balatonalmádi (lecture)

3. G. Peintler, **B. Kormányos**, A. Nagy, I. Nagypál
   Kinetics of Reaching the Equilibrium State in Iron(III)- and Sulphate Containing Solutions.
   Royal Society of Chemistry, Inorganic Reaction (poster, abstract)
   Mechanisms Meeting 2003, Athens, Greece